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To cite this article: J. Zhou *et al* 2011 *EPL* **95** 27002

A Letters Journal Exploring the Frontiers of Physics

July 2011

EPL, **95** (2011) 27002
doi: 10.1209/0295-5075/95/27002

www.epljournal.org

Vacancy or not: An insight on the intrinsic vacancies in rocksalt-structured GeSbTe alloys from ab initio calculations

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received 26 April 2011; accepted in final form 26 May 2011
published online 27 June 2011

PACS 71.15.Mb – Density functional theory, local density approximation, gradient and other corrections
PACS 71.15.Nc – Total energy and cohesive energy calculations
PACS 61.72.Bb – Theories and models of crystal defects

Abstract – Rocksalt-structured GeSbTe (GST) phase-change materials contain significant amounts of intrinsic vacancies at one sublattice. On the basis of *ab initio* total energy calculations, we have shown that the so-called intrinsic vacancies result from geometrical voids that originate from packing spaces for lone pairs of electrons tightly bound to specific Te layers where a weak bonding exists. The existence of such geometrical voids is concomitant with a narrow band gap. The present results will shed new insights on the intrinsic vacancies in rocksalt-structured GST.

Pseudo-binary mGeTe-$n$$Sb_2Te_3$ (GST, m and n are integers) alloys are important phase-change materials used as record media for optical data storage, and are currently investigated for applications in phase-change random access memory (PRAM) that is considered as one of the most promising next-generation memory devices [1–3]. The rewritable data storage is achieved by the extremely fast and reversible phase transition between amorphous and rocksalt-structured GST. For the rocksalt-structured GST, it is accepted that Te occupies one sublattice and Ge, Sb and vacancies occupy the other sublattice of the rocksalt structure. In the past years, quite a lot of works have been carried out to understand the atomic and vacancy configurations in GST [4–12]. For the atomic arrangements, some early works assumed a random occupation of Ge, Sb and vacancies at one sublattice of the rocksalt structure [4,5]. Later, by a high-resolution transmission electron microscopy study, Park *et al.* reported an ordered rocksalt structure for $Ge_2Sb_2Te_5$ (GST225), where the Ge and Sb atoms alternatively positioned themselves on specific {111} planes [10]. This result was supported by our *ab initio* calculations [8]. For the role of vacancies, Wuttig *et al.* suggested that vacancies can reduce the antibonding states in GST on the basis of *ab initio* calculations [7], however, the "vacancies" they investigated were manually removed from rocksalt-structured GeTe, which can hardly represent the intrinsic vacancies of GST that result from the stoichiometry.

In this work, by *ab initio* total energy calculations and using $Ge_2Sb_2Te_5$ (GST225) and $Ge_1Sb_2Te_4$ (GST124) as prototypes, we show that the so-called intrinsic "vacancies" in rocksalt-structured GST are geometrical voids that originate from packing spaces for lone pairs of electrons tightly bounded to specific Te layers where weak bonding exists.

Our *ab initio* total energy calculations were based on density functional theory (DFT) in conjunction with the projector-augmented-wave (PAW) pseudopotentials within the generalized gradient approximation (GGA91) which are implemented in the VASP code [13,14]. The tetrahedron method with Blöchl corrections was used and the k points of $7 \times 7 \times 5$ were automatically generated by the method developed by Monkhorst and Pack [15,16].

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Table 1: The calculated cohesive energy (in eV/atom) and equilibrium volume (in $\mathrm{\AA}^3$/atom) for S_1-GST (E^0_{S1}, V^0_{S1}) and after relaxation S_{1r}-GST (E^r_{S1}, V^r_{S1}) as well as that for S_{2r}-GST (E^r_{S2}, V^r_{S2}). Herein $E_f = E^r_{S1} - E^0_{S1}$ (in eV/Va, Va denotes one vacancy), $V_f = V^r_{S1} - V^0_{S1}$ (in $\mathrm{\AA}^3$/Va, Va denotes one vacancy).

Phases	E^0_{S1}	V^0_{S1}	E^r_{S1}	V^r_{S1}	E_f	V_f	E^r_{S2}	V^r_{S2}
GST_{225}	−3.645	27.27	−3.795	30.87	−1.35	32.4	−3.797	30.99
GST_{124}	−3.569	27.27	−3.760	32.06	−1.31	33.5	−3.757	31.94

The structures were fully relaxed with respect to both lattices and atomic positions.

It is known that by optimizing an initial atomic configuration using DFT the lowest energy structure for this atomic configuration is obtained. Therefore, we first constructed some atomic configurations and then perform *ab initio* calculations for stable structure searching. A complete random arrangement of Ge, Sb and vacancies has been shown not to be energetically favorable in our previous work [8], and is thus not considered here to simplify the calculations. The initial structures are constructed based on the (111) plane and along the [111] direction from the rocksalt-structured GeTe. The initial lattice parameter a is assigned to be 6.02 Å and the structure consists of building units of -Te-Ge- and -Te-Sb-Te-Te-Sb-Te- [8]. In this case, there are two possibilities to keep the above building blocks. One is that some Te will occupy Na positions and some Ge and Sb will occupy Cl positions (referred to as S_1-GST hereafter), *i.e.*, antisite layers in the rocksalt structure. The other is that some Na layers were removed in order to keep Ge, Sb and vacancies at Na sites and Te at Cl sites (referred to as S_2-GST hereafter), *i.e.*, the building blocks consisting of building units of -Te-Ge-Te-Sb-Te-Va-Te-Sb-Te- (Va denotes vacancy) [8]. The structures for S_1-GST225 and S_2-GST225 which respectively contain 18 and 27 atoms can be illustrated by figs. 3(a) and (c). The rule to build S_1-GST124 and S_2-GST124 is similar to GST225, which are not thus shown here for brevity. A 21-atom cell was used for both S_1-GST124 and S_2-GST124. Then the S_1-GST and S_2-GST structures were all under full relaxation in terms of atomic positions and volumes by *ab initio* total energy calculations. The structures after full relaxation are denoted as S_{1r}-GST and S_{2r}-GST, respectively.

Table 1 lists the calculated results; it is seen that the cohesive energy and equilibrium volume of S_{1r}-GST are very close to that of S_{2r}-GST. For example, the differences in energy and volume between S_{1r}-GST225 and S_{2r}-GST225 are only 2 meV/atom and 0.12 $\mathrm{\AA}^3$/atom, respectively, and between S_{1r}-GST124 and S_{2r}-GST124 they are 3 meV/atom and 0.12 $\mathrm{\AA}^3$/atom, respectively. The structure feature of S_{1r}-GST225 is also very close to that of S_{2r}-GST225. Furthermore, if we define the formation energy of a vacancy as the energy difference between a crystal with a vacancy and a perfect crystal, containing the same number of atoms [17], we obtained negative values for the formation energy of one vacancy in both GST225 and GST124 (table 1). In addition, the energy required to form one vacancy in GST225 is similar to that in GST124. The results demonstrate that rocksalt-structured GST alloys without vacancies are less stable and forming vacancies is energetically favorable.

Table 2: The interlayer distances of (111) planes along the [111] direction for S_1-GST, S_{1r}-GST and S_{2r}-GST.

	$d_{Te\text{-}Te}$ (Å)	$d_{Ge\text{-}Te}$ (Å)	$d_{Sb\text{-}Te}$ (Å)
S_1-GST_{225}	1.738	1.738	1.738
S_{1r}-GST_{225}	3.109	1.734, 1.688	2.034, 1.713
S_{2r}-GST_{225}	3.144	1.750, 1.677	2.055, 1.730

Assuming the formation volume of one vacancy as the volume difference between a crystal with a vacancy and a perfect crystal, both containing the same number of atoms [17], we obtain formation volumes of a monovacany for GST225 and GST124 being 32.4 and 33.5 $\mathrm{\AA}^3$ (table 1), respectively, which is large enough to accommodate one Ge or Sb atom since the volume of one Ge or Sb atom is 8.18 or 12.77 $\mathrm{\AA}^3$, providing we take the atomic radius for Ge and Sb being 1.25 and 1.45 Å [18], respectively. Further analysis on the (111) interlayer distances (table 2) shows the position of the "vacancy" volume. The (111) interlayer distances of $d_{Te\text{-}Te}$, $d_{Ge\text{-}Te}$ and $d_{Sb\text{-}Te}$ in S_1-GST225 are 1.738 Å. While in S_{1r}-GST225, significant changes occurred between adjacent Te layers, with the distance increasing from 1.738 Å to 3.109 Å after a full structure relaxation, which agrees with that of S_{2r}-GST225. On the other hand, although longer and shorter interlayer distances were obtained for the Ge-Te and Sb-Te layers in S_{1r}-GST225, the average interlayer distances of $d_{Ge\text{-}Te}$ and $d_{Sb\text{-}Te}$ are 1.701 Å and 1.873 Å, respectively, which are close to that in S_1-GST225. The results clearly show that the "vacancy" volume locates between adjacent Te layers. Therefore, the so-called "vacancy" may not be a missing atom position, but a geometrical void. The following analysis of density of states (DOS) and electron localization function (ELF) [19] will shed light on the issue of its origin.

Figures 1(a) and (b) show the total DOS for GST225 and GST124, respectively. The most striking feature in fig. 1 is that there is no band gap at the Fermi level for S_1-GST, while an energy gap of ~ 0.5 eV opens for both S_{1r}-GST225 and S_{1r}-GST124, which coincides with S_{2r}-GST. Therefore, the opening of this energy gap which lowers the total energy (table 1) is the driving force for

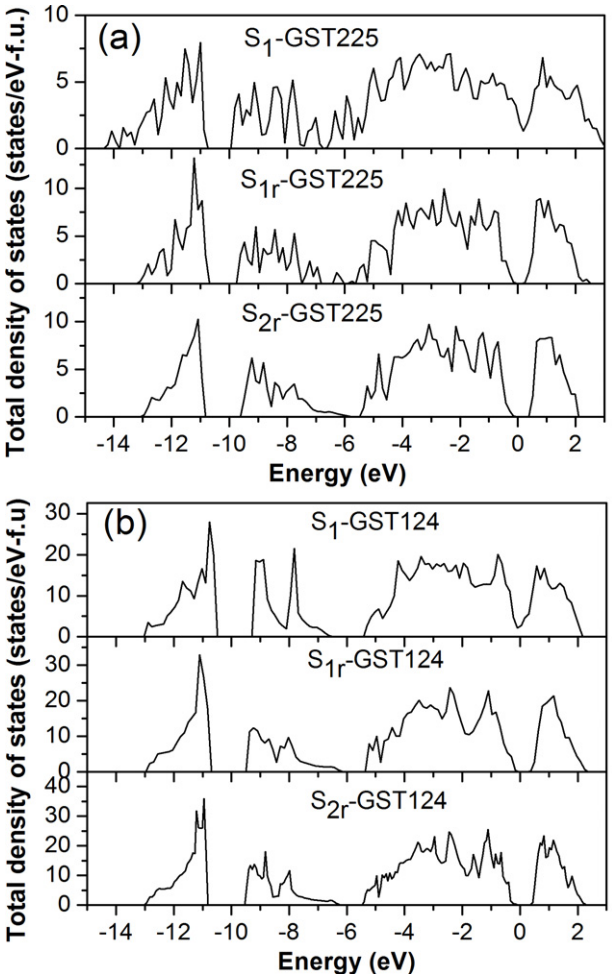

Fig. 1: Total density of states for S_1-GST, S_{1r}-GST and S_{2r}-GST: (a) GST225, (b) GST124. The Fermi level is set to zero.

the formation of vacancies in GST. In other words, the existence of "vacancy" or geometrical void in GST resulted from the opening of a band gap at the Fermi level and the reduction of total energies. Quite interestingly, the opening of an energy gap in the electronic density of states was considered as the driving force for the structural reorganization into the amorphous state of GeSb [20].

On the basis of topological analysis of the ELF [21], which is a very useful sensor for problems in structure determination [19], we gained deep insight into the nature of vacancies in GST. Figures 2(a) and (b) show the ELF sections through a plane showing all the typical bonding in S_1-GST225 and S_{1r}-GST225, respectively. The obvious feature in fig. 2 is that the chemical bonding in GST225 is a strong covalence. The bonding isosurface completely envelops the nonbonding isosurface that displays as a banana shape at the center of the bonding isosurface for Te and Sb atoms and roughly spherical isosurface for Ge atoms. The most interesting feature is between adjacent Te layers, as seen in fig. 2(a), the interaction between adjacent Te layers is strong covalent in S_1-GST225, while in S_{1r}-GST225 there is no direct

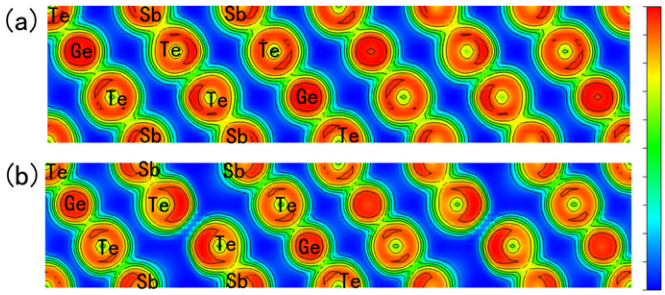

Fig. 2: (Color online) Contour plots of ELF showing typical chemical bonding for (a) S_1-GST225, (b) S_{1r}-GST225. The scale is from 0 (blue) to 1 (red) and the interval is 0.14.

bonding between the Te and Te atoms (fig. 2(b)), which is the same as that in S_{2r}-GST225 (not shown here for brevity). The calculated bond energy between adjacent Te layers for S_{2r}-GST225 is 5.30 meV/atom, suggesting that the bonding between the Te layers might be very weakly van der Waals like. However, this statement has to be further testified by a more proper method like GW due to the limitation of pure DFT in accurately describing the electron correlations and the van-der-Waals–like physical bonding. The same analysis is applied to GST124 alloy.

To unravel the origin of the "vacancy" or geometrical void between adjacent Te layers, ELF is also used to identify the position of lone pairs of electrons since in electron-rich compounds, such as GST, lone pairs of electrons could play an important role in the formation of structures [19]. For this purpose, isosurfaces corresponding to ELF values at 98% of the local maximum ones are analyzed as this 98th percentile view can provide a picture of the ELF isosurface in the nonbonding region [22]. For GST225, the values of the local maxima of ELF increases from 0.8804 in S_1-GST225 to 0.9099 in S_{1r}-GST225 that is close to 0.9101 in S_{2r}-GST225, which suggests that the chemical bonding character of S_{1r}-GST225 is similar to that of S_{2r}-GST225. The same analysis is applied to GST124. To obtain a clear picture of position of the nonbonding regions, the ELF isosurfaces generated at the 98th percentile [22] for S_1-GST225, S_{1r}-GST225 and S_{2r}-GST225 are displayed in fig. 3. It is interesting to note that for S_1-GST225 (fig. 3(a)) the 98th percentile of spherical-shaped isosurface mainly locates at Ge with very few locating at Te atoms, while for S_{1r}-GST225 (fig. 3(b)), the 98th percentile of banana-shaped isosurface locates at specific Te where weak Te-Te bonding exists. This coincides with that of S_{2r}-GST225 (fig. 3(c)). The position of the 98th percentile ELF isosurface suggests that lone pairs of electrons locate between adjacent Te layers with a banana shape in rocksalt-structured GST [22]. These lone pairs of electrons might be the origin of the existence of geometrical void or "vacancies" in rocksalt-structured GST, *i.e.*, vacancies in GST are generated for an electronic reason as a packing space for lone pairs of electrons that are tightly bound to the specific Te atoms. The existence of lone pairs of electrons also endows the Te atoms with high

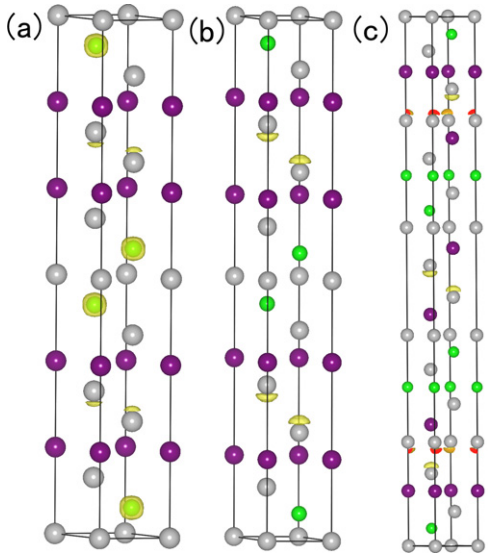

Fig. 3: (Color online) 98th percentile ELF isosurfaces generated for the nonbonding regions for (a) S_1-GST225, (b) S_{1r}-GST225 and (c) S_{2r}-GST225. The green spheres represent Ge, the purple ones represent Sb and the grey ones represent Te.

activity as well as weak bonding between them, which may play a significant role in the fast reversible phase transition process.

In conclusion, based on the present results, the so-called intrinsic vacancies in GST are geometrical voids that originate from packing spaces for lone pairs of electrons tightly bounded to specific Te layers where weak bonding exists. Even though the present model is rather ideal, the results indicate that the lone pairs of electrons tightly bound to the specific Te atoms may be a specific character of GST phase-change materials. Therefore, it would be beneficial to consider this feature when tailoring the properties of GST or searching new materials with better performances.

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This work is partially supported by National Natural Science Foundation of China (60976005), the Outstanding Young Scientists Foundation of Fujian Province of China (2010J06018) and program for New Century Excellent Talents in University (NCET-08–0474). The State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Micro-System and Information Technology (CAS) is also acknowledged. RA thanks VR Sweden.

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